β-Alkoxy- and Aryloxypropionates

By C. E. Rehberg and Marion B. Dixon

Earlier papers from this Laboratory described *n*-alkyl β-ethoxypropionates,[2] *n*-alkyl β-*n*-alkoxypropionates[3] and a group of β-alkoxypropionates of various types.[4]

The present paper, which concludes this series, describes the addition of various alcohols and phenols to the olefinic group in acrylic esters and the alcoholysis of some of the resulting ether-esters. Table I shows the new compounds and their characteristics.

Table I

Preparation, Properties and Analyses of Esters, $ROCH_2CH_2COOR'$

R	R′	Yield, %	Boiling point °C.	Boiling point Mm.	$n^{20}D$	d^{20}_4	Mol. refraction Calcd.	Mol. refraction Found	Sapn. equiv. Calcd.	Sapn. equiv. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl	Isobutyl	44[a]	88	29	1.4128	0.9349	42.44	42.70	160.2	161.3	60.0	59.9	10.1	10.1
Methyl	3-Chloropropyl	78[b]	82	2	1.4402	1.1207	42.69	42.50	...	...	46.5	47.0	7.3	7.5
Ethyl	3-Chloropropyl	75[b]	80	1	1.4400	1.0843	47.31	47.33	...	...	49.3	49.0	7.8	7.8
Ethyl	2-Chloroallyl	84[b]	45	0.4	1.4448	1.0952	46.85	46.84	192.6	182.7	49.9	49.7	6.8	6.7
Phenyl	Ethyl	53[a]	92	.7	1.5002	1.0745	52.69	53.17	194.2	188.6	68.0	68.0	7.3	7.6
Phenyl	Methyl	59[a]	85	.4	1.5071	1.1076	48.08	48.44	180.2	171.4	66.6	66.3	6.7	6.8
p-Cresyl	Methyl	37[a]	91	.4	1.5061	1.0811	52.69	53.37	...	...	68.0	68.1	7.3	7.3
o-Cresyl	Methyl	52[a]	92	.8	1.5042	1.0797	52.69	53.27	194.2	190.5	68.0	67.8	7.3	7.2
Methyl	2-Ethoxyethyl	86[a]	92	6	1.4225	1.0094	44.08	44.40	176.2	175.5	54.5	54.4	9.1	8.9
Methyl	2-Phenoxyethyl	53[b]	112	0.2	1.5010	1.1118	58.96	59.44	224.3	223.5	64.2	64.2	7.2	7.2
Methyl	Tetrahydrofurfuryl	68[b]	74	0.3	1.4459	1.0796	46.50	46.47	188.2	189.2	57.4	56.6	8.6	8.5
Furfuryl	Methyl	30[a]	127	12	1.4693	1.1278	45.57	45.52	184.2	191.5	58.7	58.5	6.6	6.5
2-Ethoxyethyl	Methyl	57[a]	70	1.2	1.4232	1.0128	44.08	44.32	176.2	172.4	54.5	54.6	9.1	8.9
2-Ethoxyethyl	2-Ethoxyethyl	57[a]	96	0.2	1.4307	1.0114	59.58	59.93	234.3	235.9	56.4	56.3		
n-Butyl	2-Methoxyethyl	87[b]	68	.5	1.4253	0.9719	53.32	53.79	204.3	203.3	59.0	58.6	9.9	9.9
n-Butyl	2-Butoxyethyl	62[b]	100	.5	1.4298	0.9415	67.17	67.54	246.3	244.5	63.4	63.4	10.6	10.3
Ethyl	2-(2-Chloroethoxy)-ethyl	79[b]	96	.3	1.4451	1.1153	53.57	53.64	112.4	113.6	48.1	47.9	7.6	7.6

[a] Made by the addition of alcohol to the acrylic ester. [b] Made by the alcoholysis of $ROCH_2CH_2COOR$ where R = CH_3, C_2H_5 or C_4H_9.

It was of interest that phenols reacted better than most primary alkanols of comparable molecular weight.[3] Furfuryl alcohol and 2-ethoxyethanol also reacted satisfactorily.

From this and previously reported studies it may be concluded that most unhindered primary alkanols and phenols readily add to acrylic esters, the activity being less with compounds of higher molecular weight. Secondary alcohols are generally less reactive than the primary ones. Tertiary alcohols appear to be unreactive.

Alcoholysis of lower alkyl esters of ether-acids is a convenient way to prepare higher esters, as may be seen from the yields in Table I.

The detailed procedures used in the present work have been described in an earlier paper.[4]

Summary

Seventeen esters of β-alkoxy- and β-aryloxypropionic acids have been prepared by (a) addition

(1) One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) Dixon, Rehberg and Fisher, This Journal, **70**, 3733 (1948).

(3) Rehberg, Dixon and Fisher, *ibid.*, **69**, 2966 (1947).

(4) Rehberg, Dixon and Fisher, *ibid.*, **68**, 544 (1946).

of alcohols or phenols to alkyl acrylates, or (b) alcoholysis of a lower alkyl ester of the appropriate ether-acid. The order of activity in (a) was phenol > primary alcohol > secondary alcohol. Tertiary alcohols did not react.